# *Ab-Initio* Cluster Calculations of Hole Formation and Trapping in $PbF_2$ and $PbF_4$[*]

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## *Abstract*

We have used *ab-initio* quantum chemistry computer codes to model the formation of holes and the energy barriers for their diffusion in two lead fluoride hosts of potential interest for scintillation—$PbF_2$ and $PbF_4$. The crystals were modeled by $Pb_{24}F_{48}$ and $Pb_{14}F_{56}$ atomic clusters embedded in arrays of several thousand point charges to reproduce the Madelung potential to an accuracy of several mV throughout the cluster. Cubic $PbF_2$ has the same crystal structure as $CaF_2$, however their electronic structures are different. It is known experimentally that in $CaF_2$ holes travel easily along rows of F atoms which accounts for the high luminous efficiency of the scintillator $CaF_2$:Eu. In contrast, these calculations show that in $PbF_2$ holes are trapped on the Pb atoms by an energy barrier of ~1 eV. This result is consistent with the failure of $PbF_2$ as an activated scintillator. Similar calculations on the experimentally unexplored crystal $PbF_4$ predict that the holes are trapped on F atoms with an energy barrier of ~1 eV and is therefore not a promising host for an activated scintillator. These computational techniques can be applied to other crystals to find those with mobile holes for new heavy-atom scintillators and solid-state detectors.

## I. INTRODUCTION

This work is motivated by the need for better gamma ray detectors for medical imaging, specifically ultra-fast bright scintillators for time-of-flight positron emission tomography, ultra-bright scintillators for gamma-ray imaging, and heavy-atom solid-state detectors with mobile carriers.

In the past, many useful new scintillators were discovered by knowledge of the luminescence literature [1] and a certain amount of intuition and luck. However, an area of critical importance for scintillators is the transfer of ionization energy to the luminescent site, a process specific to excitation by ionizing radiation, and one of the least understood [2]. In a luminous activated scintillator, electrons and holes produced during the ionization event diffuse efficiently through the host crystal and recombine at or near the activator atom to produce useful light. (For recent developments and reviews of the literature on scintillators and scintillation processes, see references [2-5].)

In this work we investigate whether available *ab-initio* quantum chemistry computer codes and high performance computers can be used to model these energy transfer processes well enough to help guide the experimental search for new scintillators. The formation of holes and the energy barriers for their diffusion are calculated using atomic clusters embedded in arrays of several thousand point charges to simulate the crystal. For efficient, rapid transfer of energy from an ionizing event to an activator atom, the barriers must be small.

$CaF_2$:Eu is a known scintillator with high luminosity. However, all attempts to activate cubic $PbF_2$ (same crystal structure as $CaF_2$) as a scintillator have failed [6]. Because large, clear crystals of $PbF_2$ are dense and can be produced at low cost, it is tempting to speculate whether the addition of the right activator could make $PbF_2$ as luminous as the brightest scintillators known (e.g., NaI:Tl, CsI:Tl, CsI:Na, $CaF_2$:Eu) or whether there is some fundamental limitation to its efficiency. We have therefore studied $PbF_2$ and $PbF_4$, a thus far experimentally unexplored material.

## II. COMPUTATIONAL METHODS

To investigate scintillation processes, the crystal is modeled by a central cluster of atoms (constructed using only unit cell information) embedded in a lattice of point charges chosen to provide the same electrostatic ionic field (Madelung potential) as in the infinite crystal. Solving the Schrödinger equation for the system of atoms and point charges determines the energy of the system and the electron density distribution. In practice, heavy atoms—desired in gamma ray detectors—are modeled by effective core potentials (that include the relativistic effects experienced by the inner electrons) surrounded by valence electrons. This reduces the computational labor because the Schrödinger equation is solved only for the non-relativistic valence electrons. The first level of theory is the Hartree-Fock (HF) method, which minimizes the energy by varying the molecular orbitals of the individual electrons one at a time (assuming at each step that the others are frozen). The molecular orbitals are linear combinations of Gaussian basis functions selected by the user. In a subsequent step, second-order Møller-Plesset (MP2) corrections can be performed on the Hartree-Fock molecular orbitals to determine an energy correction that partly accounts for electron motion correlation, however these were not applied in the present study.

In the neutral ground-state crystal, the above calculation should produce a minimum energy when the atoms are in their normal lattice positions. However, when an electron is abruptly removed in an ionization event, neither the electronic nor the atomic configurations are at a minimum energy. To find the minimum energy configuration of the resulting hole

state, the electronic wavefunction is assumed to find its minimum energy in a time that is short compared to the motion of the atoms (Born-Oppenheimer approximation). The atomic coordinates are then varied to minimize the energy; at each value of the atomic coordinates the Schrödinger equation is solved to determine the electronic structure and the energy of the system. The result is the relaxed electronic and atomic configuration after an electron has been removed (i.e., a lattice relaxed hole).

To determine whether the hole can move in the host crystal, a cluster of atoms is used that is large enough to model a self-trapped hole located at two (or three, depending on symmetry) equivalent neighboring positions. If it can be shown that the hole can move among these locations, then the hole can diffuse throughout the host crystal. After determining the atomic configurations for a self-trapped hole at those locations, ideally the configuration space is searched to find the minimum energy path from one hole to the next. In this work, a simple average of the coordinates was used. The maximum energy along the path is the energy barrier for hole diffusion. If this energy barrier is less than kT (0.025 eV at room temperature), holes diffuse readily; if the energy barrier is very much greater than kT, the holes are trapped and not able to diffuse.

To perform these calculations, the Jaguar program (Schrödinger, Inc., Portland, OR, www.schrodinger.com) was used to solve the Schrödinger equation at the Hartree-Fock level. We previously developed and successfully tested several computational techniques to model hole formation and transport in CsI [7]. Clusters of 24 Pb and 48 F atoms for $PbF_2$ and of 14 Pb and 56 F atoms for $PbF_4$ were used. To simulate a crystalline environment, it is necessary to provide a finite set of point charges that accurately reproduces the electrostatic potential of the infinite crystal lattice in the cluster volume. This was done by constructing a $2N \times 2N \times 2N$ lattice of unit cells, assigning cluster atoms to the central volume and point charges to the rest. The outermost point charge values were then varied to reproduce the Madelung potential in the cluster volume to an accuracy of a few mV. The 6-31G basis set was used for the F atoms and the LAV3P basis set and relativistic effective core potentials (provided by

the Los Alamos National Laboratory as a standard feature of Jaguar) was used for the Pb atoms. Atomic charges and electron populations were determined from the Natural Population Analysis (NPA) phase of the Natural Bond Orbital (NBO) analysis [8]. The Jaguar runs were performed on Silicon Graphics, Inc. computers with a total of twelve R10000 processors.

## III. HOLE FORMATION AND TRANSPORT IN THE CRYSTAL $PbF_2$

Cubic lead fluoride has the calcite lattice structure. Preliminary calculations of a $Pb_8F_{16}$ cluster embedded in 6,120 point charges showed that (1) in the ground state the occupied orbitals with the highest energy are on the Pb atoms, (2) when an electron is removed the hole is centered on a single Pb atom, and (3) moving a pair of neighboring F atoms from a Pb with a hole toward a neighboring Pb atom causes the hole to transfer to the second Pb atom. This is understandable, because when the two F atoms are moved toward a nearest Pb, it becomes energetically favorable for that Pb atom to have the extra positive charge. This situation differs significantly from the two-atom $V_k$ center found in some alkali halide crystals where the positive charge is shared between two halide ions.

The electron population analysis for this cluster also showed that the Pb and F atoms are not fully ionized, and had charge values of +1.8 and –0.9 respectively. For subsequent calculations, these values were used for the point charges.

A larger $Pb_{24}F_{48}$ cluster was then designed to allow the hole to occupy two equivalent nearest neighbor Pb sites (Figure 1). The four-electron Los Alamos basis set $(6s^2 6p^2)$ and associated 78-electron effective core potentials was used for the Pb atoms and the 6-31G+ basis set was used for all F atoms. The most diffuse Gaussian basis functions had exponential coefficients of 0.06 $Bohr^{-2}$ and 0.10 $Bohr^{-2}$ for the Pb and F atoms, respectively. This cluster was embedded in 11,928 point charges that reproduced the Madelung potential to an accuracy of 2.2 mV rms over the atomic cluster volume.
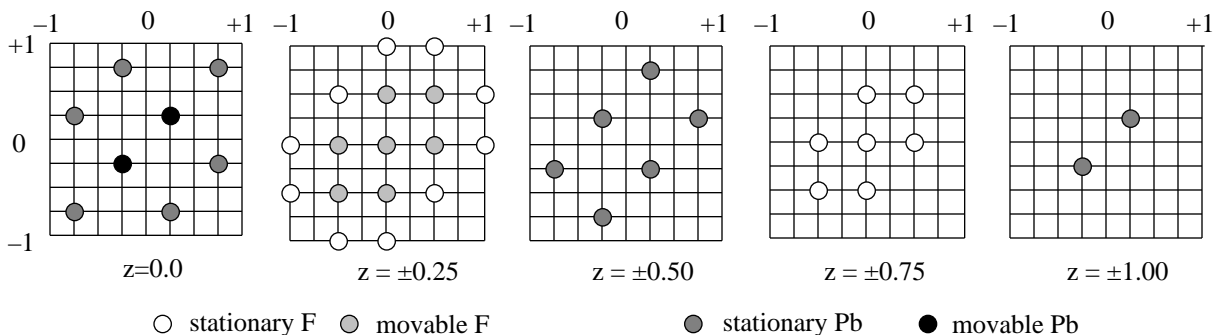


Figure 1. Schematic diagram of the Pb and F atomic layers of the $Pb_{24}F_{48}$ cluster used to model hole transport in $PbF_2$. Dimensions are in units of the unit cell parameter $a_x = b_y = c_z = 5.94$ Å.

With an electron removed and the central two Pb atoms and all their nearest eight F atoms (a total of 16 atoms) relaxed, the electron population analysis showed that the hole is centered on a single Pb atom, where 0.76 of an unpaired electron spin is on the Pb atom and the remaining unpaired spin is shared almost equally by the eight nearest neighbor F atoms. During the relaxation of the hole, the two movable Pb atoms increase their separation slightly from 4.20 Å to 4.29 Å while the eight F atoms nearest the hole are drawn in to the Pb hole center, their separation from the Pb decreasing from 2.57 Å to 2.33Å.

To investigate the transfer of a hole on one Pb to a nearby Pb, we introduce a configuration coordinate defined to be 0.0 for the relaxed hole on one Pb atom and 1.0 for the relaxed hole on the neighboring Pb atom. The calculated energies of the intermediate configurations are shown in Figure 2.
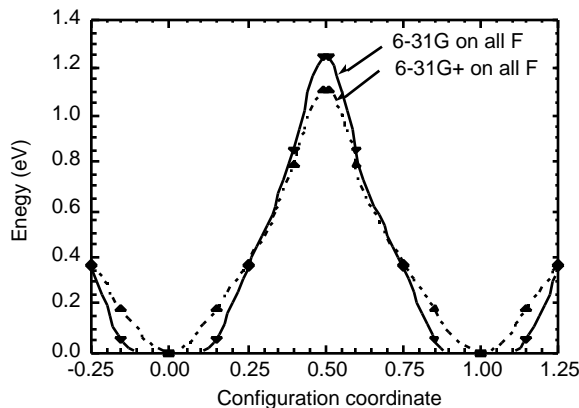


Figure 2. Calculated energy barrier for transfer of a hole on one Pb atom at 0.0 to a neighboring Pb atom at 1.0 in $PbF_2$.

When the calculation was performed with a 6-31G basis set for the F atoms (most diffuse exponential coefficient 0.35 Bohr$^{-2}$), the results (Figure 2) are close to those using the G-31G+ basis set (most diffuse exponential coefficient 0.10 Bohr$^{-2}$). In Figure 2, as the configuration coordinate increases from 0 to 0.49 the energy rises 1.11 eV above that of the relaxed hole and the electron population analysis shows that only 0.01 of an electron spin is transferred to the nearest neighbor Pb atom. At a coordinate value of 0.5, the configuration and the wavefunction is symmetric and the hole is shared equally between the two Pb atoms. However, this constraint results in a higher energy, 1.46 eV above that of the relaxed hole. For coordinate values above 0.5, the hole "hops" to the nearest neighbor Pb atom and the energy curve is symmetric about 0.5. The electron population analysis of the charge associated with each atom is consistent with the above spin analysis.

While photoluminescence has been observed from several activator atoms in crystals of $PbF_2$, scintillation has not [6]. This may be attributed to the large barrier for hole transport to the activator.

## IV. HOLE FORMATION AND TRANSPORT IN THE CRYSTAL PBF4

In contrast to Pb(II) which has two 6s outer electrons, Pb(IV) has a filled 5d outer shell and no 6s electrons. We have explored $PbF_4$ as a possible scintillator. (Other examples of Pb(IV) compounds are of the form $A_2PbF_6$, $A_2PbO_3$, $BPbF_6$ and $BPbO_3$, where A is a monovalent atom and B is a divalent atom.)

The $PbF_4$ crystal has a tetragonal lattice structure consisting of alternating planes, one containing Pb and F atoms (stoichiometrically $PbF_2$) and one containing only F atoms. The Pb atoms has six-fold nearest-neighbor F coordination, two in the F-only plane and four in the Pb-F plane. There are two different F sites, those in the F-only plane have two nearest neighbor Pb atoms (2.12 Å) and 12 nearest neighbor F; those in the Pb-F plane have one nearest neighbor Pb (1.97 Å) and 12 nearest neighbor F. The F atoms in the F-only plane are more weakly bound (10.8 eV) than those in the $PbF_2$ plane (13.8 eV). Preliminary calculations of a $Pb_7F_{34}$ cluster embedded in 8,599 point charges showed that (1) in the ground state the occupied orbitals with the highest energy are associated with F atoms in the F-only planes and (2), when an electron is removed, the hole is centered on a single F atom in an F-only plane.

The electron population analysis for this cluster also showed that the Pb and F atoms are not fully ionized, and had charge values of +3.2 and –0.8 respectively. For subsequent calculations, these values were used for the point charges.

A larger $Pb_{14}F_{56}$ cluster was then designed to allow the hole to occupy two equivalent nearest neighbor F sites in an F-only plane (Figure 3). These two F atoms had 18 nearest neighbor F atoms and 2 nearest neighbor Pb atoms; a total of 22 atoms were allowed to move in the lattice relaxations. The four-electron Los Alamos basis set and associated effective core potentials was used for the Pb atoms and the 6-31G basis set was used for all F atoms except for the central two F atoms where the 6-31G+ basis set was used to provide a better description of any covalent bond between those two F atoms. The most diffuse Gaussian basis functions had exponential coefficients of 0.06 Bohr$^{-2}$ and 0.10 Bohr$^{-2}$ for the Pb and F atoms, respectively. This cluster was embedded in 8,570 point charges that reproduced the Madelung potential to an accuracy of 0.5 mV rms over the atomic cluster volume.

When the ground state cluster was constructed from the International Crystal Structure Database (Gmelin Institute, Germany) and allowed to relax, it was found that the atoms in the F-only plane reduced the bond length to their nearest neighbor Pb atoms from 1.97 Å to 1.85Å. To provide a stable structure that preserved the configuration of the F-only plane, it was necessary to decrease the crystal constant $c_z$ from its database value of 8.03Å to 7.54 Å. It is possible that if the ten 5d Pb electrons were treated as quantum electrons rather

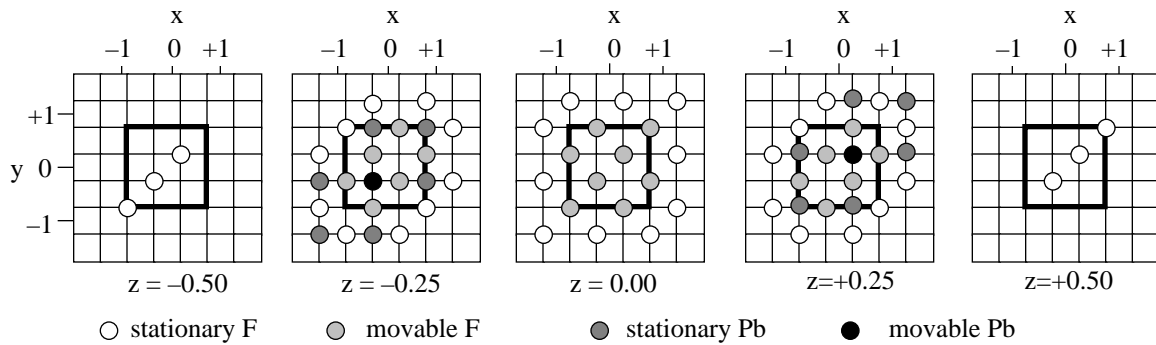than an effective core potential, the interatomic forces would    be more accurate.



Figure 3. Schematic diagram of the Pb and F atomic layers of the $Pb_{14}F_{56}$ cluster used to model hole transport in $PbF_4$. Dimensions are in units of the unit cell parameter $a_x = b_y = 4.247$ Å, $c_z = 7.54$Å.

To investigate the transfer of a hole on one F to a nearby F, we again introduce a configuration coordinate defined to be 0.0 for the relaxed hole on one F atom and 1.0 for the relaxed hole on the neighboring F atom in the F-only plane. The calculated energies of the intermediate configurations is shown in Figure 4. As the configuration coordinate increases from 0 to 0.49 the energy rises 1.11 eV above that of the relaxed hole and only 0.01 of an electron spin is transferred to the nearest neighbor F atom. At a coordinate value of 0.5, the configuration and the wavefunction is symmetric so that the hole is shared equally between the two F atoms. However, this constraint results in a higher energy, 3.15 eV above that of the relaxed hole. For coordinate values above 0.5, the hole "hops" to the nearest neighbor F atom and the energy curve is symmetric about 0.5. The electron analysis of charge associated with each atom is consistent with the above spin analysis.
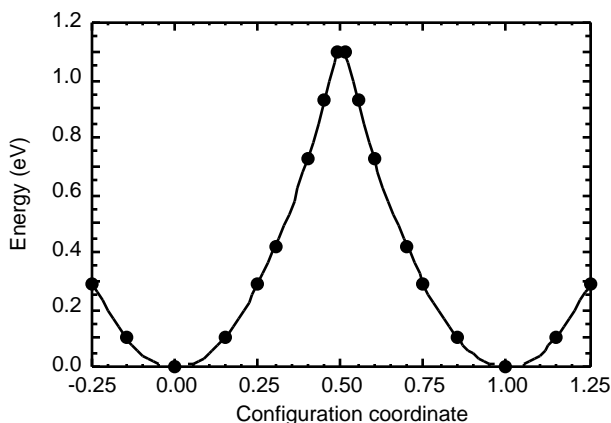


Figure 4. Calculated energy barrier for transfer of a hole on one F atom at 0.0 to a neighboring F atom at 1.0 in $PbF_4$.

Because of the large energy barrier for hole diffusion between F atoms in $PbF_4$, this material does not appear promising as a host compound for efficient activated scintillation.

## V. SUMMARY

Although it is clearly desirable to use larger clusters of atoms involving more complete ion relaxation, a larger number of basis functions, a quantum mechanical treatment of a larger number of outer electrons, and calculations at the highest feasible level of theory, these aspirations are severely limited by computation time. Nevertheless, the present *ab-initio* molecular orbital calculations have shown the following:

- A missing electron (hole) in $PbF_2$ is bound to a Pb atom.

- A missing electron (hole) in $PbF_4$ is bound to a F atom.

- In both $PbF_2$ and $PbF_4$ the calculated energy barrier for hole transport is ~1 eV.

While these results explain why $PbF_2$ has never been activated as an efficient scintillator and predict that $PbF_4$ cannot be activated, the application of these computational techniques to other Pb(IV) crystals may identify new candidates with mobile holes for further testing.

## VI. ACKNOWLEDGMENTS

company or product name does not imply approval or recommendation by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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